6. Annexes

6.1. Annex 1: Method 1 - Nutrient mass balance models for river systems, a German approach

Two methodologies are described, the German (Annex 1) and the Danish approach (Annex 2). The OSPAR HARP guideline 9 on retention methodologies will be further elaborated, and these approaches can be used where appropriated.

The knowledge about the pathways of nutrient discharges/losses from point and diffuse sources enables the quantification of the total discharges/losses of nutrients into a river system. If the nutrient discharges/losses are known, the retention can be quantified approximately as the difference between the discharges/losses and the monitored load at the river mouth. This approach entails errors due to up-scaling and insufficient knowledge about the hydrological processes in the catchment area. In the following, it is assumed that retention processes mostly cause the difference between the observed load (L) and total discharges/losses (D).

In **Germany**, an analysis has been carried out with data on the discharges/losses and riverine loads of nutrients in 100 different rivers, located in different parts of Europe. The geographical region covered by these rivers is between the Loire in France (west), the Drau in Austria (south) and the Vataanjoki in Finland (north and east), which could be find in Behrendt & Opitz (1999). River catchment areas smaller than 100 km² have not been considered.

The model requires the following parameters for the quantification of the retention:

1. the catchment area (A in km²);
2. the water-flow (Q in m³/s); and
3. the area of surface waters within the river catchment area (A_s in km²).

The area of the surface water in the catchment area (A_S) can be calculated from detailed statistics on land use or by using the surface area of the lakes and reservoirs (A_{Lake}), on the basis of land use maps (e.g. CORINE Land-cover) and the river surface by the following equation:

$$A_S = A_{LAKE} + 0.001 \cdot A^{1.185} \quad \text{[km²]} \qquad (1)$$

As = area of surface waters;
A_{LAKE} = area of lakes in the catchment; and
A = catchment area.

The second part of the sum is derived from the analysis of different river systems according to the stream order (Billen et. al., 1992; Billen et al., 1995), and measurements in rivers of different size (see also Behrendt & Opitz, 1999). The parameters in this equation should be developed specifically for the region/catchment under consideration.

For river systems with many artificial ditches in floodplains and humid climate the approach of Equation (1) can be modified according to Behrendt et al. (2003) by the following formula:

$$A_S = A_{LAKE} + 0{,}0052 \cdot A^{1.09} \cdot SL^{-0.278} \quad \text{[km²]} \qquad (2)$$

SL = the mean slope within the catchment area.

The application of the different approaches to catchment areas of plains in southern Europe has shown that the approaches described in Equations 1 and 2 have to be modified because the area of surface waters will be probably overestimated (Schreiber et al. 2003).

As shown by Vollenweider & Kereekes (1982), the relationship between the discharges/losses of nutrients into the lake and the state of the lake can be described by the following equation:

$$\frac{C_{N,P}}{C_{INPUT_{N,P}}} = \frac{1}{1 + R_{SN,SP}} \tag{3}$$

$C_{N,P}$ = the nutrient concentration observed in the lake;
$C_{INPUT\ N,P}$ = the nutrient concentration in the inflow; and
$R_{SN,SP}$ = the specific retention of nutrients.

The specific retention ($R_{SN,SP}$) is estimated by the statistical analysis of lakes in different regions of the world, and appears to be dependent on the residence time of the lakes. Equation (3) can be generalised for a river system with or without lakes by the following equation:

$$\frac{L_{N,P}}{I_{N,P}} = \frac{1}{1 + R_{SN,SP}} \tag{4}$$

$L_{N,P}$ = the nutrient load at a certain monitoring station;
$D_{N,P}$ = the sum of all nutrient discharges/losses within the catchment area upstream of this monitoring station; and
$R_{SN,SP}$ = the specific retention of nutrients.

The specific retention is a quantity without dimensions. To date, there appears to be no estimations of the residence time of the water in a whole river system. The quantification of nutrient retention in inland surface waters (both lakes and rivers) is therefore derived from other relevant parameters. Kelly et al. (1987) and Howarth et al.(1996) have shown that the nitrogen retention of lakes and rivers is dependent on the hydraulic load (HL; defined as the annual run-off divided by the water surface of the river basin). In the form of equation (4) this model can be written by the following equation:

$$\frac{L_N}{D_N} = \frac{1}{1 + \frac{S_N}{HL}} \tag{5}$$

S_N = the average mass transfer coefficient given in m/a.

Behrendt & Opitz (1999) found that the specific nitrogen and phosphorus retention of river systems depends on the hydraulic load and/or specific run-off (q: defined as the run-off divided by the area of the river basins). The following relation between the specific retention of the hydraulic load and the specific retention were proposed:

$$\frac{L_{N,P}}{D_{N,P}} = \frac{1}{1 + a \cdot HL^b} \quad \text{or} \quad \frac{L_{N,P}}{D_{N,P}} = \frac{1}{1 + a \cdot q^b} \tag{6}$$

The coefficient of the model of Equation (6) is the same as S_N for nitrogen, if the coefficient b is –1. The coefficients of both models were estimated on the basis of 100 different river basins in Europe. The results are given in Table 1.1, for total phosphorus and dissolved inorganic nitrogen according to Behrendt & Opitz (1999) as well as for total nitrogen according to Behrendt et al. (2003).

Table 6.1: Results of regressions between the nutrient retention per load (R_L) of river systems and the specific run-off (q) and the hydraulic load (HL) for the studied river systems. A, B are the factors for the non-linear multiple regression and N is the number of measurements included in the calculation.

	q	**HL**[1]
Total Phosphorus:		
r^2	0.8090	0.6148
N	89	89
A	26.6	13.3
B	-1.71	-0.93
Dissolved inorganic Nitrogen:		
r^2		0.6535
N		100
A		5.9
B		-0.75
Total Nitrogen:		
r^2		0.521
N		56
A		1.9
B		-0.49

[1] Results of a model according to Equation (6).

The models explain more than 60% of the total variance of the L/D ratio (load/discharge) for both, phosphorus and nitrogen. According to equations (5) and (6), the models can be applied to river systems and lakes, if the surface water area (A_S) and the water flow (Q) are known. Further values of the coefficients for river basins grouped by the basins' size are given in Behrendt & Opitz (1999).

The procedures described above concern river catchment areas larger than 50 km². The data set used for the development of the model represents the situation of different river catchment areas over a longer time period. Therefore, the models cannot be used for the description of inter-annual fluctuations in one river system. The application of the retention models is only given for inland surface waters with a hydraulic load and a specific run-off larger than 1 m/year and 3 l/(km²·s), respectively.

Within the last years the model approaches were enlarged for total nitrogen, therefore table 1 includes coefficients of the retention model for both: total nitrogen and dissolved inorganic nitrogen (DIN = NO_3 + NH_4 + NO_2). The difference between the calculated load of dissolved inorganic nitrogen (DIN) and total nitrogen (TN) especially for rivers with low hydraulic load is the transfer of nitrogen from dissolved forms into particulate material by primary production.

Equation (5) and (6) enable the estimation of the nitrogen and phosphorus load in cases where the area is non-monitored and the discharges/losses are calculated at source according to chapter 3 of these Guidelines. The total nitrogen and phosphorus retention in inland surface waters ($R_{N,P}$) can be estimated by multiplication of the observed or calculated nitrogen and phosphorus loads with the specific retention of nitrogen and phosphorus according to equations (4) and (5) and/or (6).

$$R_{N,P} = R_{SN,SP} \cdot L_{N,P} \quad (7)$$

$R_{N,P}$ = total nitrogen and phosphorus retention in inland surface waters;
$R_{SN,SP}$ = the specific retention of nitrogen and phosphorus; and
$L_{N,P}$ = the nitrogen and phosphorus load at a certain monitoring station.

In combination with a model for the estimation of the nutrient discharges/losses into river systems, the retention approaches where applied for a lot of larger and medium catchment areas in Europe (Axios, Danube, Daugva, Elbe, Motala, Odra, Po, Rhine, Rhönne A, Vistula, Weser). From these applications it can be concluded that the approaches for nitrogen can be applied for real river systems as well as for catchment areas with a mix of lakes and rivers. For phosphorus however, the approaches does not correctly estimate the retention if larger lakes and reservoirs are occur. Depending on the characteristic of the lakes (polymictic or dimictic) and the location of the lakes within the catchment area the retention will be over- or underestimated. These problems can be solved by a separation of the catchment areas into sub-catchment areas for lakes and river systems. For the retention of dimictic lakes the Vollenweider formula can be applied. For river systems without large lakes the approaches for the phosphorus retention is well functioning.

Vink & Behrendt (2002) have also applied the coefficients for the retention of heavy metals according to equation (6).